

# Degradation of Monoethanolamine Used in CO<sub>2</sub> Capture from Flue Gas of a Coal-Fired Electric Power Generating Station

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## Abstract

Combustion of fossil fuels is responsible for about 85% of the world's energy supply. It is also the most significant source of carbon dioxide (CO<sub>2</sub>) emissions worldwide. Due to concern about the effect of CO<sub>2</sub> emissions on global climate, as well as the world's great dependence on fossil fuels, it is becoming increasingly important to develop economically feasible technology to capture and sequester CO<sub>2</sub> from fossil fuel burning power plants. One of the highest priorities in carbon sequestration science is the development of techniques for CO<sub>2</sub> separation and capture, since it is expected to account for the majority of the total cost (~75%). The most common currently used method for CO<sub>2</sub> separation is reversible chemical absorption using monoethanolamine (MEA) solvent. A problem with this technique is associated with the degradation of the MEA by processes that are not completely understood. This degradation leads to increases in material costs, waste disposal costs, and energy demands for the CO<sub>2</sub> capture process. In order to limit or eliminate MEA degradation, it is important to first understand the chemical reactions involved in the process. With this goal in mind, samples were obtained from the IMC Chemicals Facility in Trona, California, a plant that has been performing CO<sub>2</sub> capture from flue gas since 1978. These samples, which consist of MEA taken from various stages of the CO<sub>2</sub> capture process, were analyzed to identify the products of solvent degradation. The results of these analyses as well as a discussion of the possible mechanisms leading to MEA degradation are presented.

## Introduction

Increasing awareness of the possible influence of greenhouse gases on global climate change has led to recent efforts to develop strategies for the reduction of carbon dioxide (CO<sub>2</sub>) emissions (U. S. DOE, 1999; Herzog et al., 1997). One such strategy that has received a great deal of attention involves the capture of CO<sub>2</sub> from large point sources (such as fossil fuel-fired power plants) and the long-term storage underground or in the ocean. However, there is a great concern over what impact such a plan would have on electricity prices (Herzog, 1999; Leci, 1997; Meisen et al., 1997). Since CO<sub>2</sub> comprises less than 20% of flue gas from conventional fossil fuel combustion processes, it would be impractical and cost prohibitive to

compress and store the total flue gas output from a boiler. Therefore, it is important to separate the CO<sub>2</sub> from other flue gas constituents prior to storage. This CO<sub>2</sub> separation and capture step is expected to make up the majority (up to 75%) of the expense for a carbon sequestration process (Herzog, 1999).

Although there are several different methods that have been proposed for the capture and separation of CO<sub>2</sub>, the only method that has been proven to work on an industrial scale is chemical absorption using monoethanolamine (MEA) as a solvent (Herzog, 1999). In this method, MEA absorbs CO<sub>2</sub> through chemical reaction in an absorber column. Since the reaction is reversible, the CO<sub>2</sub> can be driven off by heating the CO<sub>2</sub> rich amine in a separate stripper column. The MEA may be recycled through the process. For the low CO<sub>2</sub> partial pressure present in flue gas, alternative methods of CO<sub>2</sub> removal are less efficient and more expensive than chemical absorption (Herzog, 1999).

There are alternative approaches to electrical power generation, such as integrated coal gasification combined cycle (IGCC), which produce a higher pressure and higher concentration stream of CO<sub>2</sub> (Seabright et al., 2001; Doctor et al., 2001; Tam et al., 2001). This allows the use of a less energy intensive, less expensive method than chemical absorption for CO<sub>2</sub> separation. However, the great majority (>90%) of new power plants that are projected for construction in the U. S. by 2020 as well as most existing plants produce flue gas at one atmosphere (U. S. EIA, 2001). Clearly, if a significant reduction in CO<sub>2</sub> emissions is to be achieved, chemical absorption will need to play an essential role.

A major problem associated with chemical absorption using MEA is the degradation of the solvent through irreversible side reactions with CO<sub>2</sub> and other flue gas components (Polderman et al., 1955; Chi et al., 2001; Rooney et al., 1998). This leads to numerous problems with the process. First, degradation of MEA results in solvent loss, requiring the replacement of up to 8 pounds of MEA per ton of CO<sub>2</sub> captured (Arnold et al., 1982). It is also known to lead to foaming (Kohl et al., 1985), fouling (Chakma et al., 1987; Yagi et al., 1992), and increased viscosity (Polderman et al., 1955) of the amine. In existing CO<sub>2</sub> capture facilities, the degradation products are separated in an evaporative reclaimer and disposed of as hazardous chemical waste (Barchas et al., 1992).

In the case of carbon sequestration, the most significant problem presented by MEA degradation is associated with increased corrosion caused by the degradation products (Polderman et al., 1955; DeHart et al., 1999). In order to keep machinery corrosion rates at an acceptable level, the concentration of MEA must be kept low (typically under 20% for coal boilers and ~30% for natural gas-derived flue gas and then only if corrosion inhibitors are employed). Low MEA concentration reduces the effectiveness of the solvent, necessitating large equipment sizes and faster circulation rates. In addition, more energy is required in the stripping column in order to regenerate the amine (Leci, 1997). This increased “parasitic load” is of particular concern for carbon sequestration. In addition to being an additional cost, producing this extra energy leads to increased CO<sub>2</sub> emissions, which decreases the overall benefit of sequestration (Herzog, 1999). A sensitivity analysis indicates that increasing the

concentration of MEA to 70% will cut the parasitic load on a power plant by more than half (Leci, 1997).

Although CO<sub>2</sub> separation using MEA is a relatively mature technology, the process has not been optimized for the abatement of CO<sub>2</sub> emissions from fossil fuel-fired power plants (Yagi et al., 1992; Chakma, 1997). Its primary uses have been the sweetening of natural gas streams (Kohl et al., 1985) and the commercial production of CO<sub>2</sub> from flue gas (Arnold et al., 1982; Sander et al., 1992). Because of the increased concern with efficiency and the parasitic load on a plant, decreasing the role of solvent degradation is a much more important issue to sequestration than to previous applications of the MEA process.

The current study is aimed at developing an increased chemical understanding of MEA degradation processes. Increased insight into the mechanisms and chemical pathways associated with MEA degradation may result in decreasing or eliminating its negative effects. There have been several previous studies on reactions of alkanolamines with O<sub>2</sub> (Rooney et al., 1998), CO<sub>2</sub> (Polderman et al., 1955; Yazvikova et al., 1975), COS (Dawodu et al., 1994), or CS<sub>2</sub> (Dawodu et al., 1996). Most of these studies were aimed at understanding natural gas sweetening processes, and all were conducted under laboratory conditions. However, in flue gas from a fossil fuel-fired boiler, the process becomes much more complicated due to the presence of a mixture of CO<sub>2</sub>, O<sub>2</sub>, CO, SO<sub>x</sub>, NO<sub>x</sub>, fly ash, and other constituents. The degradation process in this case remains poorly understood, particularly under conditions that are common to power plants (Meisen et al., 1997).

## **Experimental**

The IMC Chemicals Facility in Trona, California is a plant that has been performing CO<sub>2</sub> capture from flue gas since 1978, longer than any other such plant in the world. CO<sub>2</sub> is separated from flue gas of a coal-fired boiler, which is used to produce electricity. In this case, the captured CO<sub>2</sub> is used for carbonation of brine from Searles Lake, California for the commercial production of sodium carbonate (Arnold et al., 1982). For the current study, MEA samples were obtained from this plant in order to identify the degradation products from the CO<sub>2</sub> separation process. Two degraded samples were obtained as well as a sample of the virgin concentrated MEA. The first sample was “lean” MEA. This is the material that is introduced to the absorption column where it is contacted by flue gas. The second was a sample of the reclaimer bottoms, which represents the still bottoms that remain after the amine is distilled to remove the degradation products.

In order to identify the volatile organic compounds in the samples, each mixture was separated and analyzed using combined gas chromatography-mass spectrometry (GC-MS) and combined gas chromatography-Fourier transform infrared absorption spectrophotometry (GC-FTIR). Two separate gas chromatographic columns were used for separation. The first was a 60 m × 0.32 mm i. d. fused silica column coated with a 0.25-μm film of 14%-(cyanopropyl-phenyl)-methylpolysiloxane (DB-1701 from J&W Scientific). This column was temperature programmed from 35 to 280°C at 1 C°/min. The second column, a 60 m × 0.25 mm i. d. column coated with 0.25-μm modified polyethylene glycol (Nukol™ from

Supelco), was temperature programmed from 50 to 200°C at 5 C°/min. Helium carrier gas was used with initial linear velocities of 40 and 36 cm/s, respectively. In both cases, samples were introduced via a split injector held at 250°C. GC-MS experiments were performed using an HP 5973 mass selective detector (MSD) and GC-FTIR experiments employed an HP 5965A infrared detector (IRD).

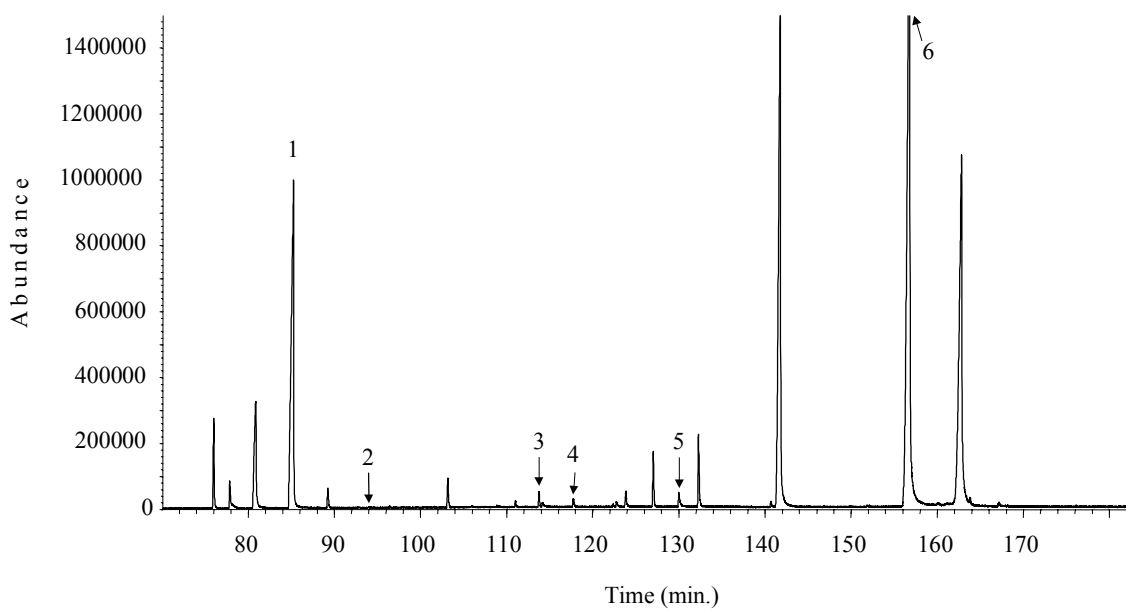
In addition, precise molecular masses of the organic compounds were obtained using low voltage high-resolution mass spectrometry (LVHRMS) (Schmidt et al., 1987). Mass spectra were acquired on a Kratos MS-50 high-resolution mass spectrometer. The ionizing voltage was set to about 11.5 electron volts in order to minimize fragmentation and therefore enhance detection of molecular ions. In this experiment, the samples were introduced to the ion source directly without prior separation.

Inorganic ionic species were identified using ion chromatography (IC) as well as combined inductively coupled plasma-atomic emission spectroscopy (ICP-AES). IC experiments were performed for anions using a Dionex DX-100 Ion Chromatograph equipped with a conductivity detector. The analytical column used was an IonPac CS14 (4 mm), and the guard column was an IonPac AG14 (4 mm). The eluent was 3.5 mM sodium carbonate/1 mM sodium bicarbonate, at a flow rate of 1.2 ml/min. A self-regenerating ASRS-Ultra (4 mm) suppressor was used. ICP-AES experiments were performed using a Perkin Elmer Optima 3000 to measure trace metal concentrations.

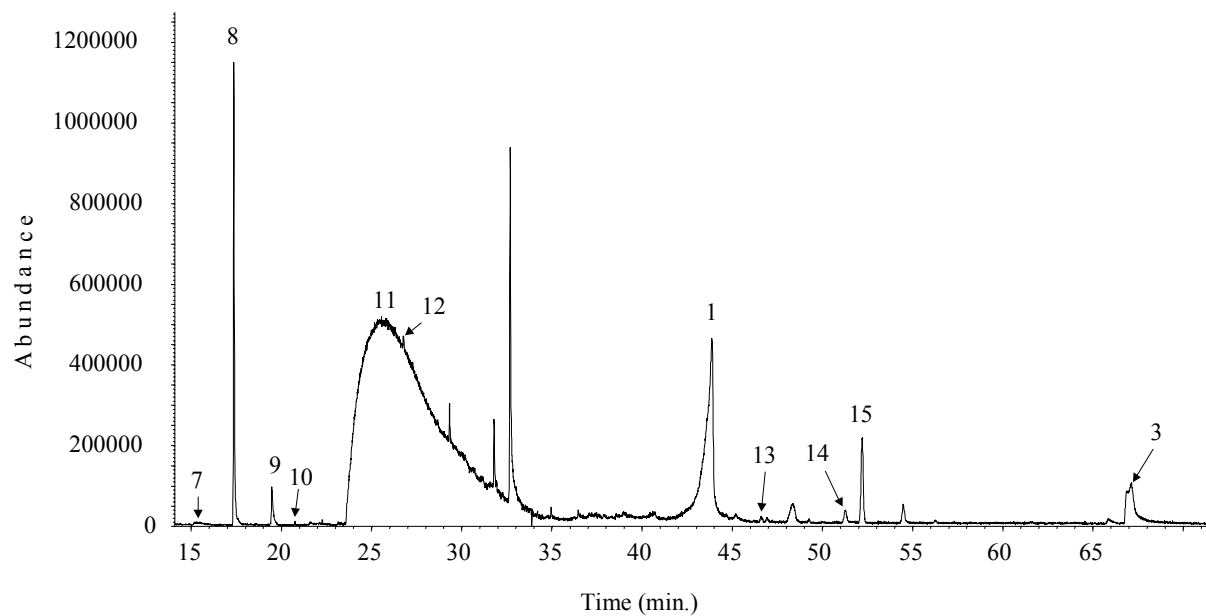
## Results

Since the focus of this study was on the MEA degradation products, the reclaimer bottoms sample, where these products were concentrated as a result of distillation provided the most important information. Portions of the total ion chromatograms obtained from GC-MS analysis of this sample on both the DB-1701 and the Nukol™ columns are shown in Figures 1 and 2, respectively. The numbered peaks are identified in Table 1 along with the methods of identification. An “x” in the GC-MS or GC-FTIR column indicates a positive match from an electronic search of either MS or FTIR libraries. MS library searches were performed using the NIST Mass Spectral Search Program for the NIST/NIH/EPA Mass Spectral Library (Stein et al., 1998). FTIR searches were performed using the FTIRsearch.com service (FTIRsearch.com, 2001). The LVHRMS column indicates whether a match within 0.003 amu of the mass of the indicated molecule was present in the mass spectrum of the entire sample. Also included in Table 1 is an indication of the column used for the experiment in which each compound was detected. The % of total area refers to the integrated peak area from the total ion chromatogram as a percentage of the total signal intensity for each chromatogram. Other than the MEA, none of the peaks shown in Figures 1 and 2 were present in identical experiments performed on the virgin MEA.

The use of two separate GC columns (one intermediate and one polar stationary phase) was necessary due to the large variation in polarity of the degradation products, a result of the large number of heteroatoms present in the compounds. This is illustrated by the fact that



**Figure 1.** A portion of the total ion chromatogram of the reclaimer bottoms sample obtained using the DB-1701 column. Numbered peaks are identified in Table 1. (MEA peak at 9.3 minutes not shown.)



**Figure 2.** A portion of the total ion chromatogram of the reclaimer bottoms sample obtained using the Nukol™ column. Numbered peaks are identified in Table 1.

each chromatogram (Figures 1 and 2) has some major peaks that are not present in the other. This is in part due to the fact that the stationary phase of Nukol™ columns incorporates acidic functional groups. This allows the column to transmit acidic compounds that might not otherwise be eluted, while absorbing basic compounds. Thus, the carboxylic acids were observed using the Nukol™ column, but not the DB-1701 column. For the same reason, the Nukol™ column does not transmit basic compounds well. They are absorbed and therefore do not appear in the chromatogram.

Peaks 5 and 15 are known degradation products of MEA resulting from reaction with CO<sub>2</sub> (Polderman et al., 1955; Yazvikova et al., 1975). These are relatively minor components. The MEA degradation products in the largest abundance are N-acetyethanolamine and N,N-diacetyethanolamine (peaks 1 and 6). This indicates that degradation may be dominated by a process other than simple reaction between MEA and CO<sub>2</sub>. The carboxylic acids (peaks 8,9, and 10) have been previously identified as products of oxygen induced MEA degradation (Rooney et al., 1998). The acetylated MEA components are believed to be the result of reaction between acetic acid and MEA.

The results of the ICP-AES and IC analyses are shown in Table 2. ICP-AES measurements were made for 23 different metal cations. Shown are seven metals that were present at no less than 0.2 ppm concentration in either of the two samples. Most prominent is the sodium concentration, mostly due to the sodium carbonate added to the reclaimer in order to regenerate MEA that has been converted to its protonated (acidic) form. Other metals are believed to originate in large part from the coal. In addition, mercury was found to be present in the reclaimer bottoms at 1.0 ppb and was not detectable in the lean MEA (<0.02 ppb).

Anion concentrations are all relatively higher, with chloride being the most significant at 4.9% (wt.). The halogens present in the samples are thought to be present as a result of simple acid/base chemistry between mineral acids (HX where X is any halogen) present in the flue gas with MEA to form “heat stable salts”. HX is the combustion product of halogens present in the feed coal. The amounts of halogen anions observed in the reclaimer bottoms parallel the halogen concentrations typically found in coal. Also, note that, with one exception, the concentration of various anions is greater in the reclaimer bottoms than in the lean MEA. This is what would be expected, since the purpose of the reclaimer is to remove contaminants from MEA and concentrate them in the bottoms. The exception is the sulfate, which is an order of magnitude more concentrated in the lean MEA than in the reclaimer bottoms. It is thought that the concentration of sulfate in the reclaimer bottoms is limited by solubility factors.

### **Future Activities**

Identification of all compounds seen in the chromatographic separations is yet to be achieved. Further experiments which are currently in progress include combined gas chromatography-atomic emission detection (GC-AED) as well as preparative GC followed by NMR spectroscopy. It is expected that the remaining compounds will be identified based on the further information that these techniques will provide.

It has been shown that oxidation of alkanolamines also leads to organic ionic species (Rooney et al., 1998), which have not yet been detected in this study. Further IC analyses, which will specifically probe organic ions, will also be performed to determine concentrations of such species.

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## Disclaimer

Reference in this report to any specific commercial product, process, or service is to facilitate understanding, and does not necessarily imply endorsement or favoring by the United States Department of Energy.

**Table 1.** Identified organic compounds from MEA reclaimer bottoms.

peak	compound	<u>method of identification</u>			<u>GC column</u>		<u>%of total area</u>	
		GC-MS	GC-FTIR	LVHRMS	DB-1701	Nukol	DB-1701	Nukol
1	N-acetyethanolamine (C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub> )	x		x	x	x	8.86	6.28
2	N-glycylglycine (C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub> )	x		x	x		<0.01	
3	N-(hydroxyethyl)-succinimide (C <sub>6</sub> H <sub>9</sub> NO <sub>3</sub> )	x		x	x	x	0.16	*
4	N-(2-hydroxyethyl)-lactamide (C <sub>5</sub> H <sub>11</sub> NO <sub>3</sub> )	x	x	x	x		0.07	
5	1-(2-hydroxyethyl)-2-imidazolidinone (C <sub>5</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> )	x	x		x		0.24	
6	N,N-diacetyethanolamine (C <sub>6</sub> H <sub>11</sub> NO <sub>3</sub> )		x	x	x		21.83	
7	ammonia (NH <sub>3</sub> )	x				x		0.10
8	acetic acid (C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> )	x		x		x		2.02
9	propionic acid (C <sub>3</sub> H <sub>6</sub> O <sub>2</sub> )	x				x		0.30
10	<i>n</i> -butyric acid (C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	x		x		x		0.01
11	monoethanolamine (C <sub>2</sub> H <sub>7</sub> NO)	x	x	x	x	x	*	35.18
12	2,6-dimethyl-4-pyridinamine (C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> )	x		x		x		0.05
13	2-imidazolecarboxaldehyde (C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O)	x		x		x		0.05
14	1-methyl-2-imidazolecarboxaldehyde (C <sub>5</sub> H <sub>6</sub> N <sub>2</sub> O)	x		x		x		0.17
15	2-oxazolidone (C <sub>3</sub> H <sub>5</sub> NO <sub>2</sub> )	x		x		x		0.80

\* Area percentage not calculated due to overlap with other peaks

**Table 2.** Ion Concentrations in ppm

	Lean MEA	Reclaimer Bottoms
<b>Cations</b>		
Sodium	80	821
Potassium	2.2	18
Calcium	1.1	1.3
Iron	1.4	1.1
Copper	0.2	0.1
Zinc	0.3	0.2
Aluminum	not detectable	0.4
Selenium	not detectable	17.4
Arsenic	not detectable	1.7
<b>Anions</b>		
Fluoride	300	1500
Chloride	1600	49000
Bromide	0.9	80
Sulfate	2200	250
Nitrate	290	3100
Nitrite	130	**
Phosphate	7.8	230

\*\* not quantified due to overlap with chloride peak



## References

- Arnold, D. S., Barret, D. A., Isom, R. H. (1982), *Oil and Gas Journal* **80** (47), 130-136.
- Barchas, R. and Davis, R. (1992), *Energy Convers. Mgmt.* **33**, 333-340.
- Chakma, A. (1997), *Energy Convers. Mgmt.* **38**, S51-S56.
- Chakma, A. and Meisen, A. (1987), *Can. J. Chem. Eng.* **65**, 264-273.
- Chi, S. and Rochelle, G. T. (2001), "Oxidative Degradation of Monoethanolamine", Presented at the First National Conference on Carbon Sequestration, Washington, D. C.
- Dawodu, O. F. and Meisen, A. (1994), *Ind. Eng. Chem. Res.* **33**, 480-487.
- Dawodu, O. F. and Meisen, A. (1996), *Gas. Sep. Purif.* **10**, 1-11.
- DeHart, T. R., Hansen, D. A., Mariz, C. L., McCullough, J. G. (1999), "Solving Corrosion Problems at the NEA Bellingham Massachusetts Carbon Dioxide Recovery Plant" presented at NACE's Annual Conference, Corrosion/99, San Antonio, Texas.
- Doctor, R. D., Molburg, J. C., Brockmeier, N. F., Manfredo, L., Gorokhov, V., Ramezan, M., and Steigel, G. J. (2001), "Life-Cycle Analysis of a Shell Gasification-Based Multi-Product System with CO<sub>2</sub> Recovery", Presented at the First National Conference on Carbon Sequestration, Washington, D. C..
- FTIRsearch.com* (2001) Galactic Industries Corp. and Thermo Nicolet Corp.
- Herzog H. (1999), "An Introduction to CO<sub>2</sub> Separation and Capture Technologies," Energy Laboratory Working Paper, Massachusetts Institute of Technology (August, 1999).
- Herzog, H., Drake, E., Adams, E. (1997), *CO<sub>2</sub> Capture, Reuse, and Storage Technologies for Mitigating Climate Change—A White Paper*, DOE Order No. DE-AF22-96PC01257, U. S. Govt. Printing Office, Washington, DC.
- Kohl, A. L., Riesenfeld, F. C. (1985), *Gas Purification; 4th Edition*, Gulf Publishing, Houston.
- Leci, C. L. (1997), *Energy Convers. Mgmt.* **38**, S45-S50.
- Meisen, A. and Shuai, X. (1997), *Energy Convers. Mgmt.* **38**, S37-S42.

Polderman, L. D., Dillon, C. P., Steele, A. B. (1955), *Oil & Gas Journal* **54**(2), 180-183.

Rooney, P. C., DuPart, M. S., Bacon, T. R.(1998), *Hydrocarbon Processing*, 109-113 (July 1998).

Sander, M. T. and Mariz, C. L (1992), *Energy Convers. Mgmt.* **33**, 341-348.

Schmidt, C. E., Sprecher, R. F., Batts, B. D. (1987), *Anal. Chem.* **59**, 2027-2033.

Seabright, J., Lee, A., Weissman, R (2001), "Environmental Enterprise: Carbon Sequestration using Texaco Gasification Process", Presented at the First National Conference on Carbon Sequestration, Washington, D. C.

Stein, S., Levitsky, A., Fateev, O., Mallard, G.(1998), *The NIST Mass Spectral Search Program for the NIST/EPA/NIH Mass Spectral Library* Version 1.6, National Institute of Standards and Technology, USA.

Tam, S. S., Stanton, M. E., Ghose, S., Deppe, G., Spencer, D. F., Currier, R. P, Young, J. S., Anderson, G. K., Le, L. A., and Devlin, D. J. (2001), "A High Pressure Carbon Dioxide Separation Process for IGCC Plants", Presented at the First National Conference on Carbon Sequestration, Washington, D. C..

U. S. Energy Information Administration (2001), *Annual Energy Outlook 2001 With Projections to 2020*, Report#:DOE/EIA-0383.

U.S. DOE (1999), *Carbon Sequestration Research and Development*, U. S. Dept. of Energy Report, (December, 1999).

Yagi T., Shilbaya H., Sasaki T. (1992), *Energy Convers. Mgmt.* **33**, 349-355.

Yazvikova, N. V., Zelenskaya, L. G., Balyasnikova L. V. (1975), *J. Appl. Chem. USSR* **48**, 699-702.